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Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel)☆

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Abstract

Biodiesel, an alternative diesel fuel derived from transesterification of vegetable oils or animal fats, is composed of saturated and unsaturated long-chain fatty acid alkyl esters. When exposed to air during storage, autoxidation of biodiesel can cause degradation of fuel quality by adversely affecting properties such as kinematic viscosity, acid value and peroxide value. One approach for increasing resistance of fatty derivatives against autoxidation is to treat them with oxidation inhibitors (antioxidants). This study examines the effectiveness of five such antioxidants, *tert*-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and α-Tocopherol in mixtures with soybean oil fatty acid methyl esters (SME). Antioxidant activity in terms of increasing oxidation onset temperature (OT) was determined by non-isothermal pressurized-differential scanning calorimetry (P-DSC). Analyses were conducted in static (zero gas flow) and dynamic (positive gas flow) mode under 2000 kPa (290 psig) pressure and 5 °C/min heating scan rate. Results showed that PrG, BHT and BHA were most effective and α-Tocopherol least effective in increasing OT. Increasing antioxidant loading (concentration) showed sharp increases in activity for loadings up to 1000 ppm followed by smaller increases in activity at higher loadings. Phase equilibrium studies were also conducted to test physical compatibility of antioxidants in SME-No. 2 diesel fuel (D2) blends. Overall, this study recommends BHA or TBHQ (loadings up to 3000 ppm) for safeguarding biodiesel from effects of autoxidation during storage. BHT is also suitable at relatively low loadings (210 ppm after blending). PrG showed some compatibility problems and may not be readily soluble in blends with larger SME ratios. Although

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α-Tocopherol showed very good compatibility in blends, it was significantly less effective than the synthetic antioxidants screened in this work.

Keywords: Antioxidant; Biodiesel; Fuel stability; Non-isothermal; Oxidation onset temperature; Oxidative stability; Phase equilibria; Pressurized-differential scanning calorimetry; Scan rate

1. Introduction

Biodiesel is an alternative fuel and extender proposed for applications ranging from on- and off-road compression-ignition (diesel) engine powered vehicles to locomotives, stationary power, heat generation and aviation fuels. Review articles by Knothe et al. [1,2], Graboski and McCormick [3] and others [4–6] have reported extensively on the technical characteristics of biodiesel. Biodiesel is a renewable fuel that is derived from domestic feedstocks; it is environmentally innocuous and safe to handle because it has a relatively high flash point; its gross heat of combustion, specific gravity (SG) and kinematic viscosity (v) are comparable to those of corresponding petroleum middle distillate fuels; and it enhances cetane number (CN), which shortens ignition delay. Biodiesel has been reported to improve antiwear properties in blends with low-sulfur No. 2 diesel fuel (D2) [3,7]. Life-cycle studies indicated that biodiesel produces nearly three times the energy required to create it and that it has a negative carbon dioxide balance [4,8]. A recent comprehensive review and analysis conducted by the U.S. Environmental Protection Agency [9] determined that biodiesel significantly reduces regulated exhaust emissions including hydrocarbons, carbon monoxide and particulate matter at all blend levels with petroleum middle distillates. Although nitrogen oxides emissions increase slightly, the increase is generally less than 5% for blend ratios up to 20 vol.% biodiesel in D2. Biodiesel has been shown to reduce polycyclic aromatic hydrocarbon and sulfur dioxide emissions and smoke opacity [1–5]. Its major disadvantages include relatively poor cold flow properties and maintaining fuel quality during long-term storage.

Biodiesel production in the United States increased from 19 million L in 2001 to 57 million L in 2002 [10]. Given current estimates for production capacity, recent attention has focused on effects of oxidation caused by contact with ambient air (autoxidation) on biodiesel fuel quality during storage. Maintaining fuel quality of biodiesel and its blends with petroleum middle distillate fuels during long-term storage presents a concern among fuel producers, suppliers and users [11–13].

Most vegetable oil and animal fat feedstocks are triacylglycerols with long-chain (C_{16}–C_{18}) fatty acid groups attached by ester linkages to a glycerol backbone. To avoid cold weather performance issues, biodiesel derived from such feedstocks must contain a relatively high concentration (80–90 wt.%) of low-melting point mono-alkyl esters; that is, biodiesel must contain 80–90 wt.% unsaturated long-chain fatty acid alkyl esters. Unsaturated organic compounds are significantly more reactive to oxidation than saturated compounds. With respect to long-chain (C_{18}) fatty acid methyl esters, polyunsaturated esters are approximately twice as reactive to oxidation as monounsaturated esters [14].

Storage stability tests on biodiesel under accelerated conditions such as elevated temperatures and purging with dry air or oxygen have shown that oxidation can affect fuel quality with respect to acid value (AV), *v* and peroxide value (PV) [15–18]. Oxidation increased both AV and *v* at 40 °C in excess of limits established for biodiesel under the American Society for Testing and Materials (ASTM) fuel standard D 6751 [19]. Although PV is not specified in the biodiesel fuel standard, this parameter influences CN, a parameter that is specified in the fuel standard. Increasing PV increases CN, an effect that may reduce ignition delay time [20,21]. One study [22] on soybean oil fatty acid methyl esters (SME) reported steady increases in AV and *v* when subjected to simulated in-use diesel engine conditions. PV first increased, then leveled off at a maximum value near 350–400 meq/kg oil. An earlier study on SME under severe thermal-oxidative reaction conditions showed a decrease in PV with increasing reaction temperature [15]. Finally, during latter stages of aging of rapeseed oil fatty acid methyl esters, analysis of *v* and turbidity data showed the presence of soluble polymeric compounds [23].

Maintaining fuel quality of biodiesel for widespread use as an alternative fuel will depend on development of technologies to increase its resistance to oxidation during long-term storage. Factors known to affect autoxidation of fatty derivatives include presence (or exclusion) of air, temperature, light, presence of antioxidants, pro-oxidants such as hydroperoxides and presence of metal catalysts [1–3,17,18,24]. Several approaches for increasing relative resistance to oxidation of fatty derivatives have been shown to be successful for biodiesel. Storage under an inert nitrogen atmosphere retarded oxidation of methyl and ethyl esters of sunflowerseed oil for storage at temperatures up to 50 °C [18]. Bondioli et al. [17] studied the effects of storage container characteristics and reported that aging of methyl esters of rapeseed oil in glass containers at 40 °C did not significantly affect fuel quality with respect to *v*, CN, SG, flash point or cold flow properties.

Treatment with oxidation inhibitors is a promising approach because it facilitates the use of existing storage tanks and fuel handling systems without requiring upgrades or re-design. Antioxidants such as *tert*-butylhydroquinone (TBHQ) or butylated hydroxytoluene (BHT) are known to retard effects of oxidation on *v*, AV and PV of biodiesel [15,18,24,25]. Other antioxidants known to improve resistance to oxidation of vegetable oils include ascorbyl palmitate, tocopherols, butylated hydroxyanisole (BHA) and propyl gallate (PrG) [26–28].

Antioxidants are typically screened in mixtures with reference oil under accelerated conditions such as elevated temperature and/or pressure, and dry air or oxygen purge. Although established methods designed for application to petroleum middle distillate fuels may be suitable for long-term storage stability tests on biodiesel, standard test methods ASTM D 4625 (Diesel Fuel Storage Stability at 43 °C) and D 2274 (Oxidation Stability of Distillate Fuel Oil [Accelerated Method]) are not well suited for rapid monitoring or spot-checking for effects of oxidation on biodiesel fuel quality [22,23,29].

Bench laboratory techniques for analysis of fatty derivatives include monitoring PV, conjugated dienes, anisidine value and carbonyls. Spectroscopic techniques include electron spin resonance, infrared, fluorescence, chemiluminescence and NMR) [30]. Automated techniques include measurement of oil stability index (OSI), the Rancimat test and weight gain by thermogravimetric analysis (TGA) [26,31].

Thermal analytical techniques such as TGA, conventional differential scanning calorimetry (DSC) and pressurized-DSC (P-DSC) have been applied in the analysis of oxidation of petroleum-based and synthetic lubricants [32–37], biodegradable lubricants [38], aviation turbine oils [39,40] and polymers [41] as well as wood rosins and nitrile rubbers [42]. These studies generally showed that P-DSC has the advantage of increasing the total number of moles of oxygen present in the cell allowing acceleration of the reaction at lower temperatures.

Cross [43] and Hassel [44] were among the first to apply DSC and P-DSC in analysis of edible fats and oils. Results from these studies in combination with studies by Tan et al. [45] showed a good correlation between isothermal induction periods measured by P-DSC (in minutes) and OSI (in hours or days). Kinetics of oxidation and thermal decomposition of soybean, rapeseed, corn, peanut and mustardseed oils have also been examined by P-DSC [42,46–49]. Kowalski [50] studied the effects of 2–10 wt.% rapeseed oil on oxidation of engine oil by P-DSC in an attempt to characterize effects of alternative fuel contamination. Perez [51] performed similar studies on alcohol-based alternative fuels.

Perhaps the first study to examine oxidation of fatty acid methyl esters (that is, biodiesel) was performed by Raemy et al. [52]. Results from that study showed that increasing temperature or degree of unsaturation decreased induction period as measured by conventional DSC. Induction period results also showed a direct correlation with results from the Rancimat test, with respect to 6–12% variation. Stavinoha and Kline [53] pointed out that P-DSC analysis is a suitable technique for screening antioxidant activity in terms of the effects of type of antioxidant and antioxidant loading (concentration) on relative resistance to oxidation of biodiesel.

Although most of the DSC and P-DSC studies cited above featured isothermal analysis of the oxidation induction time (OIT), a more rapid means for evaluating relative oxidative stability is non-isothermal (heat-ramping) analysis. Several studies have reported on the use of non-isothermal DSC and P-DSC in analysis of neat (unchanged), air-blown, epoxidized and genetically modified soybean oils [54–56] as well as lubricants and engine oils [57]. Litwinienko and co-workers [58–60] studied oxidation kinetics of ethyl esters and fatty acids of unsaturated C_{18} fatty acids and esters and reported that increasing the degree of unsaturation increases reactiveness by decreasing the activation energy for oxidation. Litwinienko et al. [61] also showed that non-isothermal DSC and P-DSC analyses were suitable for evaluating antioxidant activity in linolenic acid doped with phenolic antioxidants. Increasing BHT loading from 0.3 to 4.0 mM increased activation energy of oxidation from 73.0 to 95.8 kJ/mol.

The work reported herein evaluates four synthetic antioxidants, TBHQ, BHT, BHA and PrG, and one natural antioxidant, α-Tocopherol, for effectiveness in increasing relative resistance to oxidation of SME. Results were collected from non-isothermal P-DSC scans under 2000 kPa (290 psig) pressure in an air atmosphere. Individual antioxidants were ranked by relative activity and effects of loading were compared. Finally, physical compatibility of each antioxidant in blends of 10, 20, 30 and 50 vol.% SME in D2 was evaluated by testing phase equilibria at 30 °C.

2. Experimental

2.1. Materials

SME originally manufactured by Interchem (Overland Park, KS) was supplied by the National Biodiesel Board (NBB, Jefferson City, MO). Gas chromatographic analysis under conditions reported in an earlier work [25] indicated a fatty acid composition of 10.7 wt.% palmitic, 3.6% stearic, 22.8% oleic, 55.5% linoleic and 7.5% linolenic. Methyl oleate (99+% 9*Z*-octadecenoic acid methyl ester) and linoleate (99+% 9*Z*,12*Z*-octadecadienoic acid methyl ester) were from Nu Chek Prep (Elysian, MN). Amoco standard low-sulfur D2 fuel was obtained from the University of Illinois Urbana–Champaign. Antioxidants ±α-Tocopherol (95%) and PrG (97% 3,4,5-trihydroxybenzoic acid propyl ester) were from Aldrich (Milwaukee, WS); TBHQ (97%), BHA (9% 2-*tert*-butyl-4-hydroxyanisole, 90% 3-*tert*-butyl-4-hydroxyanisole), and BHT (99% 2,6-di-*tert*-butyl-4-methylphenol) were from Sigma (St. Louis, MO).

2.2. Methods

P-DSC analyses were conducted with a TA Instruments (New Castle, DE) model DSC 2910 fitted with an HP 2910 model high-pressure DSC cell (maximum 7 MPa). A model 5000 personal computer-based controller was used for data acquisition and determination of oxidation onset temperature (OT). Purge gas outside the cell was low-pressure nitrogen. All scans were conducted with the cell pressurized with dry air to 2000±50 kPa (290±7 psig). A spring-action purge valve was fitted to the exhaust line to keep the cell at constant pressure during heating. P-DSC analyses were conducted using hermetically sealed aluminum pans with a ~0.5-mm-diameter pinhole punched in the top cover to allow direct contact between the sample and pressurized air. This type of pan was used for two reasons: (1) tests with open solid fat index (SFI) type pans caused a build-up of varnish deposits inside the cell [25]; and (2) closed type pans have been shown to minimize diffusion effects that can interfere with analyses [62]. Samples were analyzed simultaneously with an identical empty pan. OT data reported in this work are means determined from replicate scans on three fresh samples.

In static (zero gas flow) mode, the cell was pressurized with dry air then sealed off. After the cell was equilibrated at 25 °C, it was heated with a ramp rate=5°/min to a terminal temperature of 175 °C. Scans in static mode had zero-flow air purge inside the cell. Sample mass for static mode scans was 2.8±0.35 mg.

In dynamic (positive gas flow) mode, the cell was pressurized then sealed off similar to operating in static mode. Once cell pressure was equilibrated, the inlet valve was opened wide and the outlet valve cracked slightly open to allow steady flow of air through the cell. Air flowrate was set manually to 100±10 mL/min and monitored by a calibrated gas flowmeter connected downstream from the cell outlet valve. Once air flow was established and pressure re-stabilized, the cell was equilibrated at 30 °C then heated with a ramp rate=5°/min to a terminal temperature of 195 °C. Sample mass for dynamic mode scans was 1.44±0.083 mg.

Physical compatibility studies were conducted at 30±0.5 °C using the method of phase volumes. SME-antioxidant/D2 blends were placed in mixing cylinders and equilibrated in a constant temperature bath from Neslab Instruments (Portsmouth, NH). Following an equilibration period of 3 h, solutions where solids were detected were centrifuged to confirm the results. Results were qualitatively characterized as 'OK' (no haziness or solids), 'hazy' or containing 'solids'.

3. Results and discussion

3.1. Measurement of OT

Scans plotted in Fig. 1 illustrate how oxidation onset temperature (OT) was determined from non-isothermal P-DSC heating scans in this study. The scan from static (zero gas flow) mode P-DSC analysis of neat SME was offset by +6 W/g on the Heat Flow (y)-axis to distinguish it from dynamic (positive gas flow) mode analysis. Each scan shows results for temperature of deviation, defined as an increase in heat flow exceeding a threshold value of 0.02 W/g; OT, determined by extrapolation to the baseline; and peak maximum temperature (T_P).

Mean-value OT results for neat SME determined from three replicate scans in static and dynamic P-DSC mode are shown in Table 1. Similar analyses of very pure methyl oleate

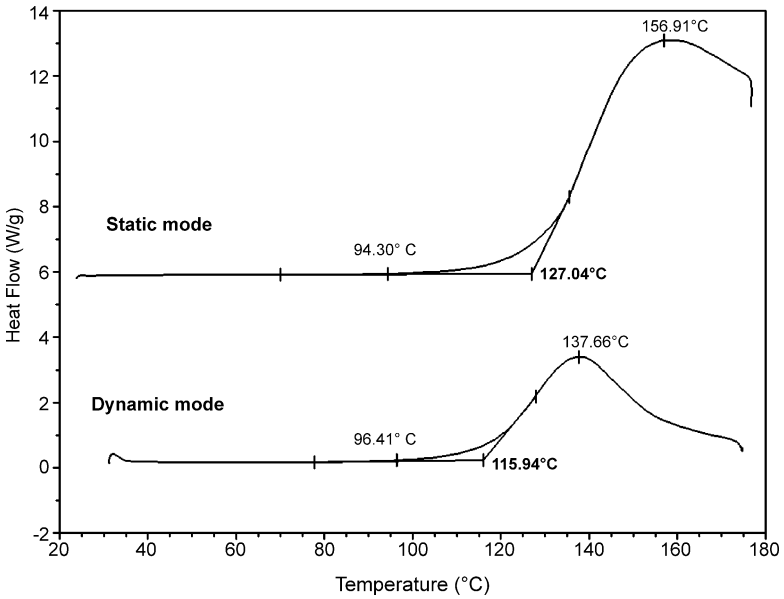

Fig. 1. Analysis of deviation (threshold=0.02 W/g), oxidation onset temperature (OT) and peak maximum temperature (T_P) of untreated soybean oil fatty acid methyl esters (SME) by pressurized-differential scanning calorimetry (P-DSC). P=2000 kPa (290 psig); ramp rate=5 °C/min. Static mode=zero gas flow. Dynamic mode=positive gas flow (100±10 mL/min air). Static mode scan offset by y=+6 W/g.

Table 1
Pressurized-differential scanning calorimetry (P-DSC) results showing effect of antioxidants on oxidation onset temperature (OT) of methyl soyate (SME)[a]

Antioxidant	Static mode[b] OT, °C	Dynamic mode[c] OT, °C
None	126±1.2	116±1.4
α-Tocopherol	146.2±0.37	128±1.6
TBHQ	157.76±0.078	137±1.0
BHA	161±2.2	149.4±0.24
BHT	157.7±0.46	151.3±0.30
PrG	161±2.4	151.2±0.84

P=2000±50 kPa (290±7 psig); Ramp rate=5 °C/min; Antioxidant loading=2000 ppm.
Mean OT values based on three replicate measurements.
[a] TBHQ=*tert*-butylhydroquinone; BHA=butylated hydroxyanisole; BHT=butylated hydroxytoluene; PrG=propyl gallate.
[b] Static mode (zero gas flow) analyses: equilibration temperature=25 °C.
[c] Dynamic mode (positive gas flow) analyses: equilibration temperature=30 °C; air flowrate=100±10 mL/min.

yielded OT=159.2±0.56 °C in static mode and 163±1.7 °C in dynamic mode. In contrast, analysis of very pure methyl linoleate yielded OT=128.2±0.47 °C in static mode and 79.0±0.98 °C in dynamic mode. If response factor (R) is defined as the ratio of OT (in K) of the sample to that of reference material, then R for neat SME was more consistent with respect to methyl oleate as a reference (R=0.92 for static mode and 0.89 for dynamic mode) than methyl linoleate (R=0.99 and 1.11).

3.2. Effect of antioxidants on OT of SME

Table 1 is a summary showing the effects of the five antioxidants studied in this work on increasing OT of SME. With respect to 2000 ppm loading for each antioxidant, both static and dynamic mode P-DSC analyses demonstrated significant increases in OT relative to untreated SME (P<0.001).

For static mode P-DSC analyses, ranking OT results in Table 1 in descending order with respect to antioxidant activity yielded the following:

$$\text{BHA} \sim \text{PrG} > \text{TBHQ} \sim \text{BHT} > \alpha\text{-Tocopherol} \gg \text{None}$$

where P=0.904 favoring BHA=PrG and 0.937 favoring TBHQ=BHT. Ranking results from dynamic mode P-DSC analyses yielded the following order:

$$\text{BHT} \sim \text{PrG} > \text{BHA} > \text{TBHQ} > \alpha\text{-Tocopherol} > \text{None}$$

where P=0.745 favoring BHT=PrG. Although dynamic mode results appeared to be similar for PrG and BHA, deviation between OT values was significant (P<0.03). Nevertheless, with the exception of BHT, order of antioxidant activity at 2000 ppm loading was generally consistent between static and dynamic mode P-DSC analyses conducted in this work.

Mittelbach and Schober [63] studied antioxidant activity in methyl fatty acid esters of rapeseed, sunflower and used-frying oils by measuring induction period at 110 °C by the

Rancimat method. Results were consistent with those reported herein with respect to PrG>BHA and (BHA, BHT, PrG, TBHQ)>α-Tocopherol, though TBHQ demonstrated better activity in the cited study than the present study. In general, results were more consistent with those from static mode P-DSC heating scans reported in this work than dynamic mode scans.

Results for PrG, BHA and BHT were consistent with those from isothermal P-DSC and non-isothermal conventional DSC studies conducted by Kowalski [64,65]. Those studies reported antioxidant activities in fresh edible oils as PrG>BHA>BHT for improving oxidative stability. Another study by Stavinoha and Kline [53] showed that BHT was slightly superior to TBHQ in mixtures with SME when tested isothermally at 125 °C and 3.45 MPa (500 psi). Those results were more consistent with those from dynamic mode P-DSC analyses in this work than static mode analyses.

Ruger et al. [66] studied antioxidant activity at very low loading (100 ppm) in soybean oil under isothermal conditions by bubbling air at 2.33 mL/s (140 mL/min) through a 20 mL liquid mixture at 105 °C. In terms of time required for the mixture to reach v=150 cP at 40 °C, antioxidant activity with respect to 100 ppm loading was TBHQ>PrG>BHT=BHA. Non-isothermal TGA studies by Gennaro et al. [67] reported BHT=BHA>untreated olive, with respect to relatively low antioxidant loadings (100–300 ppm).

Results from a previous study [25] investigating oxidation of SME by non-isothermal static mode P-DSC and isothermal OSI analyses were consistent those reported in this work. That work reported antioxidant activity with respect to 2000 ppm loading: THBQ>α-Tocopherol≫untreated SME. Another earlier work [15] reported similar results in terms of retarding effects of oxidation under accelerated conditions on AV, v and PV of SME.

Owing mostly to high volatility and relatively high susceptibility to oxidation, some phenolic antioxidants (BHA, BHT) are known to be ineffective at higher temperatures when analyzed by conventional DSC [65,68]. As discussed earlier, non-isothermal P-DSC scans for this work showed that all antioxidants were effective with respect to increasing OT relative to untreated SME (see Table 1), results that agreed with a similar study by Kowalski [64] analyzing antioxidant activity using isothermal P-DSC analyses under 1800 kPa pressure.

3.3. Comparison of static and dynamic mode P-DSC analyses

Studies on thermal-oxidation of lipids and other materials have typically focused on experimental variables such as temperature, pressure, gas type (air or oxygen), gas flowrate, heating rate, pan type (closed, standard open, open solid fat index), pan metallurgy, presence of catalysts, sample size and isothermal/non-isothermal analyses [32,35,36,42,48,62,69]. No information was found in available literature directly comparing results from static and dynamic mode DSC or P-DSC analyses.

Conducting oxidation reactions by non-isothermal analyses in a pressurized cell in static mode meant that the supply of available oxygen gradually decreased during the heating scan. In addition, closing off the pressurized cell prevented degradation products in the vapor phase from being swept away. These two conditions can decrease the driving forces for diffusion of oxygen molecules into the liquid phase and reacting with the

sample. Alternatively, analyzing the same sample in dynamic mode reduces or eliminates effects of oxygen depletion and product stagnation inside the pressurized cell, allowing driving forces for oxygen diffusion to remain nearly constant during the heating scan. Consequently, OT (and T_P) results from dynamic mode P-DSC analyses would be expected to occur at lower temperatures than from static mode analyses.

Results from this study support this hypothesis. Heating scans in Fig. 1 showed that OT and T_P from dynamic mode P-DSC analysis were 11.1 and 19.2 °C below those from static mode analysis. Results in Table 1 demonstrate this trend applied to all five antioxidants studied at 2000 ppm loading in SME as well as untreated SME. Comparison of curves in Figs. 2 and 3 showed analogous results for each antioxidant at loadings 0–5000 ppm. Between loadings of 500 and 1000 ppm, curves for BHT and PrG exhibited the smallest deviation between static and dynamic modes (<3.0 °C for BHT; <2.6 °C for PrG).

3.4. Effect of antioxidant loading on OT of SME

Curves in Fig. 2 show the effects of increasing antioxidant loading from 0 to 5000 ppm on OT measured from static mode P-DSC analyses in this study. Curves in Fig. 3 likewise demonstrate effects on OT from dynamic mode analyses.

For dynamic mode P-DSC analyses, the α-Tocopherol curve showed the smallest increase in OT relative to untreated SME. Similarly, PrG, BHT and BHA curves are very close to each other with PrG being slightly most effective at lower loadings (500–1000 ppm) and BHA being most effective at loadings near 5000 ppm. Similar results were observed for these four antioxidants for OT data determined from static mode analyses.

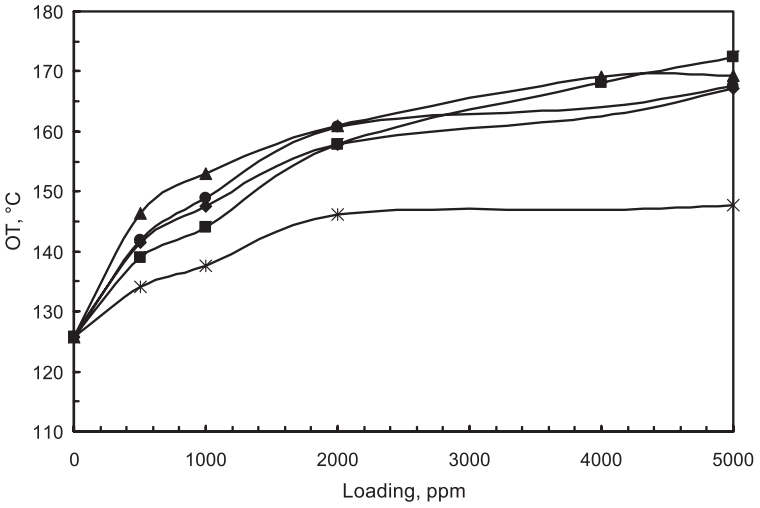

Fig. 2. Effect of antioxidant loading on OT of SME measured by static mode P-DSC analyses. *P*=2000 kPa (290 psig); ramp rate=5 °C/min. Legend: ✻=α-Tocopherol; ■=*tert*-butylhydroquinone (TBHQ); ▲=butylated hydroxyanisole (BHA); ♦=butylated hydroxytoluene (BHT); ●=propyl gallate (PrG). Variances=1.4 for untreated SME; 0.13–1.80 for α-Tocopherol; 0.0061–1.5 for TBHQ; 0.20–4.8 for BHA (exception—20 at 5000 ppm); 0.13–2.8 for BHT; 4.8–8.4 for PrG. See Fig. 1 for other abbreviations.

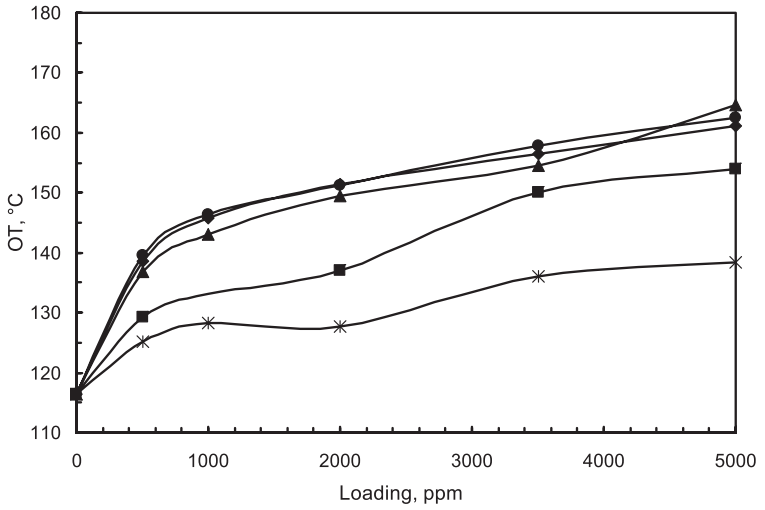

Fig. 3. Effect of antioxidant loading on OT of SME measured by dynamic mode P-DSC analyses. *P*=2000 kPa (290 psig); ramp rate=5 °C/min; air flowrate=100±10 mL/min. Legend: ✳=α-Tocopherol; ■=TBHQ; ▲=BHA; ◆=BHT; ●=PrG. Variances=1.9 for untreated SME; 0.10–2.6 for α-Tocopherol; 0.17–1.3 for TBHQ (exception—14 at 5000 ppm); 0.025–1.5 for BHA; 0.0061–1.7 for BHT; and 0.30–1.2 for PrG. See Figs. 1 and 2 for other abbreviations.

Therefore, data curves from P-DSC analysis of SME treated by antioxidants PrG, BHT, BHA and α-Tocopherol were nearly analogous in shape for both static and dynamic modes of analyses.

In contrast to comparison of curves for the other four antioxidants, a notable exception arose when comparing the TBHQ curves in Figs. 2 and 3. For OT determined from static mode P-DSC analyses, at 500 to ~1500 ppm loading, TBHQ was the second least effective antioxidant in terms of increasing OT. At higher loadings, TBHQ was much more effective and was the most effective at 5000 ppm, increasing OT by a margin of 3.3 °C greater than that of BHA. For dynamic mode analyses, TBHQ was the second least effective antioxidant at all loadings in the range 500–1000 ppm.

TBHQ is a very potent primary antioxidant for treating vegetable oil, fats and their derivatives [28]. On the other hand, TBHQ is known to lose effectiveness after aging. For this study, all static mode P-DSC analyses were carried out first followed by all dynamic mode analyses. It is possible that TBHQ lost some of its effectiveness due to aging processes that occurred during the interim between the two groups of analyses.

Data curves in Figs. 2 and 3 similarly show the largest increase in OT occurred for antioxidant loading in the range 0–1000 ppm. In most cases, increasing loading in excess of 1000 ppm caused smaller increases in OT. This behavior was similar to that of antioxidants in mixtures with edible fats and vegetable oil products where treatment at higher loadings yields little or no significant increase in activity. For example, static mode analyses of α-Tocopherol showed nearly zero increase in OT between 2000 and 5000 ppm loading. For this same example, dynamic mode analyses showed a slight increase in OT between 3500 and 5000 ppm loading. In general, these results agreed with those from

isothermal DSC studies reported by Tan and Che Man [26] and from isothermal OSI studies reported by Chu and Hsu [27].

Ruger et al. [66] reported the effects of increasing antioxidant loading from very low (100 ppm) to high (12,800 ppm) concentrations on isothermal oxidation of soybean oil. Results showed that BHT and TBHQ increased significantly while PrG decreased slightly and BHA showed no improvement. Similar to results for BHT in this study, increasing antioxidant loading changed its position in the relative order of effectiveness from least effective at 100 ppm to second most effective at 12,800 ppm loading. Raemy et al. [52] showed that increasing PrG loading in chicken fat increased oxidation induction time in both conventional DSC and Rancimat analyses.

Kowalski [64,65] showed that effectiveness of three phenolic antioxidants "levels off" towards constant or very little significant increase in activity at higher loadings in rapeseed oil. Isothermal DSC and P-DSC studies demonstrated effectiveness leveling off near 800 ppm for PrG, 1000 ppm for BHT and 8000 ppm for BHA. Litwinienko et al. [61] reported similar behavior for various phenolic antioxidants including BHT in linolenic acid. Non-isothermal P-DSC analyses showed that antioxidant activity increased sharply at low loadings then leveled off to nearly constant activity between 3300 and 8250 ppm loading for BHT and ~3700 ppm loading for both *p*-Methylphenol and 2,4,6-trimethylphenol. Mittelbach and Schober [63] also reported similar findings from investigation of the effects of increased loading of PrG, BHA, BHT and pyrogallol on isothermal oxidation of methyl esters made from rapeseed, sunflower and used-frying oils at 110 °C.

Some phenolic antioxidants (BHA, α-Tocopherol, dimethylphenol) have been shown to invert and act as a pro-oxidant at higher loadings [61,64,65,70,71]. Data curves in Figs. 2 and 3 exhibit no inversions for antioxidant loadings up to 5000 ppm. Although not shown in Fig. 2, increasing to 10,000 ppm loading did not cause inversion in activity for any of the five antioxidants investigated in this work, with respect to OT from static mode P-DSC analyses.

3.5. Physical compatibility of antioxidants in SME/D2 blends

While measuring relative activity against oxidation or autoxidation is an important aspect in the development of antioxidants for biodiesel, physical compatibility in blends of SME and petroleum middle distillate fuel is equally (if not more) important. In the field, additive packages that include antioxidants employed to safeguard biodiesel fuel quality during storage should not initiate phase separation or other transitions that cause formation of insoluble solids that can plug fuel lines and filters.

A summary of results from physical compatibility studies at 30±0.5 °C is presented in Table 2. For all blends, antioxidant loading was the concentration in SME before blending with D2. α-Tocopherol was compatible in all blends tested for loadings up to 2500 ppm, a concentration that should produce near-maximum activity in SME relative to this antioxidant. As noted in the previous section, the other four antioxidants leveled off towards nearly constant activity at higher loadings (see Figs. 2 and 3). Thus, attempts were made to test physical compatibility of these antioxidants at loadings close to where activity levels off.

Table 2
Effect of antioxidants on phase equilibria in methyl soyate (SME)-D2 blends at 30±0.5 °C[a]

Antioxidant	Loading[b], ppm	Blend ratio[c]			
		10	20	30	50
α-Tocopherol	2000	OK	OK	OK	OK
	2500	OK	OK	OK	OK
TBHQ	2000	OK	OK	OK	OK
	3000	OK	OK	OK	OK
	5000	–	solids	–	–
BHA	5000	OK	OK	OK	OK
	10,000	–	OK	–	–
BHT	2000	OK	hazy	hazy	hazy
	3000	solids	solids	hazy	OK
PrG	1000	–	OK	–	–
	3000	solids	solids	solids	hazy

Exposure time=3 h.
OK=No insoluble matter or haziness.
[a] D2=No. 2 diesel fuel (Amoco Standard); see Table 1 for other abbreviations.
[b] Mass concentration in SME before blending with D2.
[c] Vol.% SME in D2.

TBHQ was compatible in all blends tested for loadings up to 3000 ppm. However, at 5000 ppm, solids formed in the 20 vol.% blend. TBHQ is soluble in vegetable oils and fats and their derivatives; therefore, blends with higher SME ratios may be physically compatible.

BHA was physically compatible in all blends tested for loadings up to 5000 ppm and for the 20% blend at a relatively massive loading of 10,000 ppm (1 wt.%).

BHT at 2000 ppm loading was physically compatible only in the 10 vol.% blend causing haziness at higher blend ratios. In contrast, increasing loading to 3000 ppm resulted in a physically compatible mixture only for the 50 vol.% blend. These results suggest that BHT may be suitable when used at relatively low loadings for lower SME blend ratios. The 10% blend at 2000 ppm BHT had an actual antioxidant concentration of 210 ppm after blending with D2. Similar to TBHQ, BHT is soluble in vegetable oils, suggesting blends with higher SME ratios will be physically compatible. This was the case for the 50% blend at 3000 ppm BHT, which had a concentration of 1550 ppm after blending. Similarly, blends with higher SME ratios may also be physically compatible for BHT at 2000 ppm (in SME).

PrG was physically compatible in the 20 vol.% blend at 1000 ppm loading. However, increasing loading to 3000 ppm caused solids to form in the 10–30 vol.% blends and haziness in the 50% blend. PrG is poorly soluble in vegetable oils [28]; therefore, it may not show improved compatibility at higher SME blend ratios.

4. Conclusions

P-DSC analyses may be employed to evaluate antioxidant activity for improving oxidative stability of biodiesel made from transesterification of soybean oil and methanol (SME). Antioxidant activities were interpreted from OT (onset temperature) results

measured by non-isothermal P-DSC analysis. Results generally agreed with those from available literature studies on comparable DSC, P-DSC and other oxidative stability evaluation methods. Further study will be necessary to determine whether overall conclusions obtained from this work are applicable to reducing effects of oxidative degradation on biodiesel fuel quality during storage under "real world" conditions.

In general, increasing antioxidant loading (concentration) increases activity. For each antioxidant screened in this work, activity increased sharply at lower loadings (less than 1000 ppm) and by smaller increments at higher loadings (2000–5000 ppm). Curves for α-Tocopherol leveled off to nearly constant activity at loadings near 2000 ppm loading.

Curves from static (zero gas flow) and dynamic (positive gas flow) mode P-DSC analyses were similar in shape with respect to antioxidant. OT data from static mode analyses were higher in temperature than those from dynamic mode analyses due to effects of static mode conditions on hindering oxygen diffusion into the liquid phase for reaction with the sample. Results from static and dynamic mode analyses were analogous showing that PrG, BHA and BHT were most effective and α-Tocopherol least effective at increasing OT, with respect to loadings up to 5000 ppm. Anomalous results obtained for TBHQ may have been caused by its losing some potency during storage between execution of static and dynamic mode P-DSC analyses in this study.

Taking into consideration results from P-DSC analyses plus those from phase equilibrium studies on SME/D2 blends, the following recommendations are made for selection of antioxidant(s) for treating SME:

1) BHA showed very good physical compatibility and was one of the most effective antioxidants screened. It is more volatile than TBHQ (or PrG) but should be suitable as long as storage temperatures are kept low.
2) TBHQ showed good physical compatibility for loadings up to 3000 ppm (before blending) and will be among the more effective antioxidants as long as it remains potent.
3) PrG showed good physical compatibility for loadings up to 1000 ppm (before blending) and was among the most effective antioxidants screened. Its relatively poor solubility in vegetable oil derivatives may decrease its suitability for blends with higher SME ratios. More soluble gallate esters (octyl or dodecyl) may be used as alternatives.
4) BHT showed relatively poor physical compatibility but was one of the most effective antioxidants screened in this work. It may be more suitable when used in relatively small loadings (below 210 ppm concentration after blending) or in blends with higher SME ratios.
5) α-Tocopherol showed very good physical compatibility in blends but was the least effective of the five antioxidants screened in this work.

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